AFRL-SR-BL-TR-98-

0159

REPORT DOCUMENTATION PAGE

1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE
January 14, 1998

3. REPORT TYPE AND DATES COVERED
Final technical report 6/30/94-6/29/97

4. TITLE AND SUBTITLE
Deposition of Gallium Nitride Epilayers by OMVPE

5. FUNDING NUMBERS
F49620-94-1-0392

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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AFOSR/NE
Building 410
Bolling AFB, DC 20332-6448
Contract monitor: Dr. Michael Prairie

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

DISTRIBUTION STATEMENT A
Approved for public release

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Unlimited

19980218 040

13. ABSTRACT (Maximum 200 words)

Gallium nitride films have been deposited on sapphire substrates by organometallic vapor phase epitaxy and their structural quality assessed by Transmission Electron Microscopy and high resolution x-ray diffraction. The dominant type of threading dislocation was determined to be pure edge with Burgers vector 1/3 <11.0>. Dislocations are arranged into arrays corresponding to low angle twist grain boundaries with typical in-basal-plane misorientations of about 1 degree. The granular structure of the GaN film originates at the nucleation growth phase within low temperature GaN buffer. A new figure of merit for structural quality of nitride films (ϕ scan value) was proposed in order to track the amount of twist. New defects characteristic of GaN and AlGaN films have been observed and reported for the first time. These are nano-pipes or nano-tubes, empty cylinders with diameters of approximately 10 nanometers propagating along the c-axis. Nanotubes penetrate the entire film thickness and terminate in the facetted surface crater. Their density correlates with oxygen and silicon concentration in the film and can exceed 10^5 cm^{-2} in AlGaN.

14. SUBJECT TERMS
gallium nitride, epitaxy, dislocations, surface morphology

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
unclassified	unclassified	unclassified	unlimited

NSN 7540-01-280-5500

DTIC QUALITY INSPECTED 3

Deposition of Gallium Nitride Epilayers by OMVPE

Final Technical Report

AFOSR Grant F49620-94-1-0392

June 30, 1994 - June 29, 1997

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Research objectives

This grant is an augmentation Award for Science and Engineering Research Training (AASERT). Its primary objective was to modify an existing OMVPE system for deposition of gallium and aluminum nitrides, optimize the growth conditions, and assess structural quality of films. Of particular interest was the identification of different types of extended defects in nitride films and reduction of their density. The work was performed in collaboration with other faculty at Carnegie Mellon University (prof. G. S. Rohrer, D. W. Greve, and M. DeGraef) and researchers at DoD laboratories.

Summary of research performed

Nitride deposition

An existing OMVPE system designed for GaAs growth has been modified in order to deposit high quality gallium and aluminum nitride films. Modifications included fitting in a second switching manifold designed to handle hydrides, replacing single inlet reactor by two inlet reactor, and upgrading the heating from infrared lamps to induction heating. All new hardware components are controlled by the upgraded software. The deposition system in the new configuration is capable of reaching temperatures up to 1350 °C and rapid heating and cooling. The high temperature capability is expected to be essential for growth optimization of high aluminum content AlGaN suitable for solar-blind UV detectors.

GaN/Al_2O_3 growth parameters have been optimized using width of high resolution x-ray diffraction peaks and Hall effect data (both electron concentration and mobility) as figures of merit. For a 2 μm thick films, these conditions included pressure of 77 Torr and hydrogen as a carrier gas. Trimethylgallium and ammonia were used as precursors. Growth was performed on basal plane sapphire substrates that were cleaned in organic solvents, etched in a mixture of hot H_3PO_4 and H_2SO_4 and heat treated in situ in hydrogen at 1100 °C for 10 min. prior to growth. This treatment was followed by short (15 seconds) nitridation at this temperature, cooling to 500 °C and deposition of low temperature GaN buffer with nominal thickness of 20 nm. After the GaN buffers were deposited they were brought up to growth temperature of 1025 °C in ammonia flow and GaN films were grown with a growth rate of approximately 2 μm/h. The above procedure resulted in basal plane reflection FWHM of 300 arc sec, comparable asymmetric reflection width, and carrier concentrations below 10^{16} cm^{-3}. The best mobility achieved so far was 550 cm^2/Vs at room temperature.

Evaluation of structural defects in GaN/Al_2O_3

The main emphasis of this project was to evaluate the structural quality of GaN/Al_2O_3 films, determination of types of extended defects induced by lattice mismatch and differences in thermal expansion coefficient, and identification of the mechanisms responsible for nucleation of dislocations. Several significant new observations have been made and are described in detail below.

Dislocations and grain boundaries

Dislocations in GaN films have been analyzed by plan-view and cross-sectional Transmission Electron Microscopy. The dominant type of defect in the GaN films are dislocations resulting from the misfit strain introduced by the lattice mismatch between the epilayer and the sapphire substrate. The low temperature buffer is always heavily defected with individual defects very difficult to resolve due to overlapping strain fields. A defect density reduction of about an order of magnitude was observed within the initial 0.4 μm of the GaN film. At small film thickness, the dislocation lines in the GaN epilayer orient themselves irregularly. However, at film thickness larger than about 0.6 μm, most dislocations lie close to the [0001] growth direction.

A plan-view bright field image (g= $2\bar{1}\bar{1}0$) near the top surface of the GaN film is shown in Fig. 1. The defects which penetrate through the top surface of the film (they appear as dots in this particular projection) are perfect dislocations. Stacking faults were not observed in the plan-view specimens; All dislocations form short segments with similar contrast. The nature of these dislocations was studied by conventional TEM on both cross-sectional and plan-view specimens using the g·b criteria. The majority of them (which penetrate through the GaN films) were found to be pure edge, with Burgers vectors of the $1/3\langle 11\bar{2}0\rangle$ type.

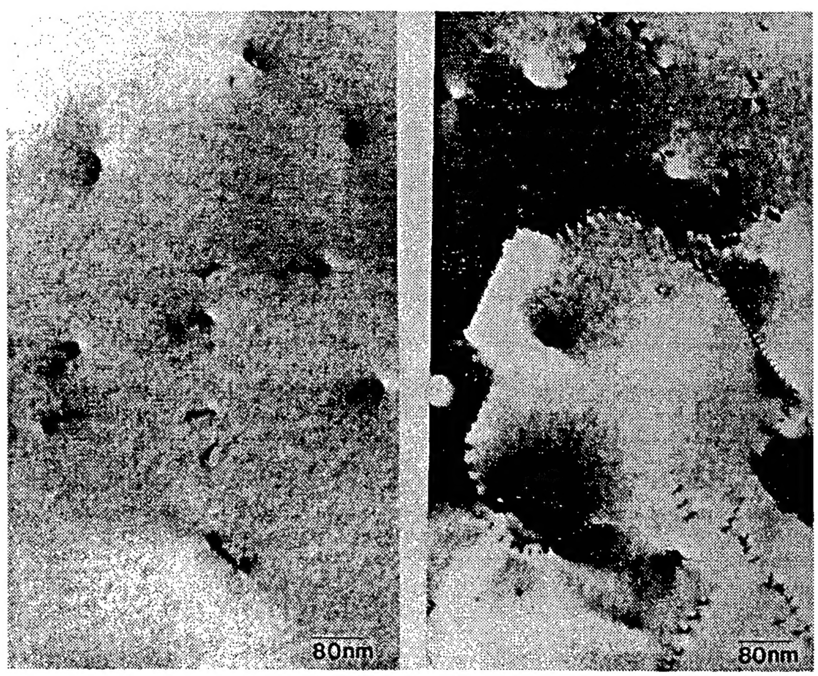

Fig. 1 Plan view bright field TEM micrograph (G=2-1.0) taken near the top of 2 μm thick GaN layer. (a) 15 seconds nitridation time (b) 3 minutes nitridation time.

Threading dislocations shown in Fig. 1 (b) form well defined arrays predominantly oriented along [11.0] directions. Frequently they were observed to form roughly closed polygonal cells with sizes from 50 to 500 nm, and the dislocation line spacing at the boundaries from 5 to 50 nm. The dislocation within the domain wall have the same Burgers vectors and wall represents a low angle grain boundary. Selective Area Diffraction patterns obtained at the grain boundaries show that the grains have in-plane misorientations of approximately 1°. Grain misorientation along the c-axis was much smaller and could not be detected by electron diffraction experiments. The x-ray rocking curves ((0004) reflection) taken on these samples have typical widths of 250-350 arc seconds. Defect density measurements carried out on plan-view specimens indicate that these grain boundaries are the main source of threading dislocations. These grains are formed during coalescence of islands at the initial stages of GaN growth, based on the nucleation mechanism first proposed by Akasaki*et al.* The AlN buffer layer is thought to have an amorphous-like structure at its deposition temperature (450 - 550 °C). Before the growth of GaN, the buffer is annealed at 1025 °C for 10 minutes, crystallizes by solid phase epitaxy, and forms columnar fine crystals. The initial growth of GaN is also columnar on top of the AlN fine crystals. During further growth, some fine crystals then become larger size islands as the result of geometric selection. Since these islands are more likely to preserve a hexagonal shape, and often have small misorientations with their neighbors, dislocation arrays are created during coalescence of these islands. These grains in a cross sectional view are delineated in Fig. 2, a weak beam image ($g=11\bar{2}0$) taken near the $[1\bar{1}00]$ orientation. The image contrast is produced by differing diffraction conditions in neighboring grains. The grain size reaches almost a constant value after a film thickness of about 0.4 μm. It is important to note that the above analysis was the first of its type for GaN/Al_2O_3 films at the time of publication (W. Qian, M. Skowronski, M. De Graef, K. Doverspike, L. B. Rowland, and D. K. Gaskill, Appl. Phys. Lett. **66**, 1252 (1995))

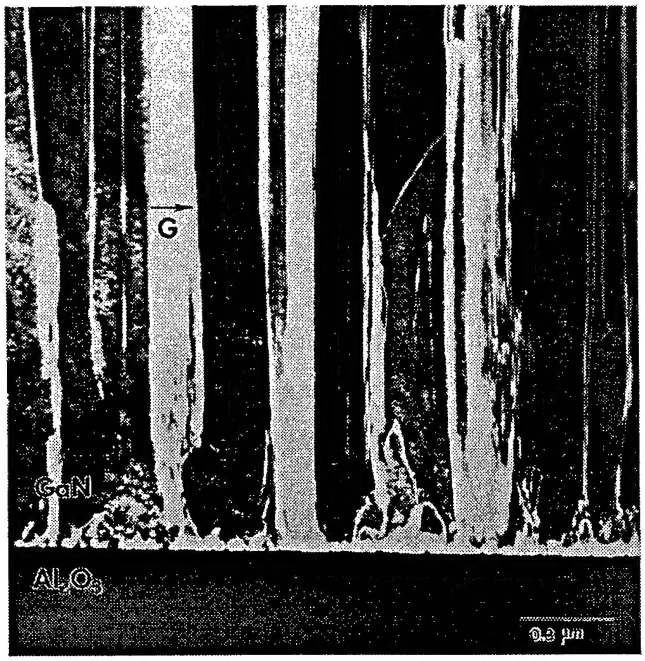

Fig. 2 Cross-sectional weak beam image of a GaN film (g=11.0) showing grain growth normal to the interface.

The dislocation density can be significantly reduced by optimizing the nitridation time of sapphire substrate. Dislocation densities below 10^9 cm^{-2} have been obtained (Fig. 1(a)). Films deposited with short nitridation times do not show a pronounced domain structure.

The width of high resolution x-ray diffraction peaks is routinely used as a figure of merit for structural quality assessment of nitride films. It was early recognized that both basal plane and asymmetric reflection widths have to be measured. However, the omega scans for either reflection cannot determine the in-plane misorientations seen in plan-view TEM. Therefore we have proposed using an additional x-ray parameter (f scan) of asymmetric reflection (10.5) as a figure of merit ("High resolution x-ray diffraction analysis of GaN-based heterostructures grown by OMVPE", M. S. Goorsky, A. Y. Polyakov, M. Skowronski, M. Shin, and D. W. Greve, Mat. Res. Soc. Symp. **449**, 489 (1997)).

Nanotubes and surface defects

In addition to dislocations, a new defect characteristic of nitride films grown on sapphire was observed for the first time (W. Qian, M. Skowronski, K. Doverspike, L. B. Rowland, and D. K. Gaskill, J. Crystal Growth **151**, 396 (1995), W. Qian, G. S. Rohrer, M. Skowronski, K.

Doverspike, L. B. Rowland, D. K. Gaskill, Appl. Phys. Lett. **67**, 2284 (1995)) and is presented in Fig. 3

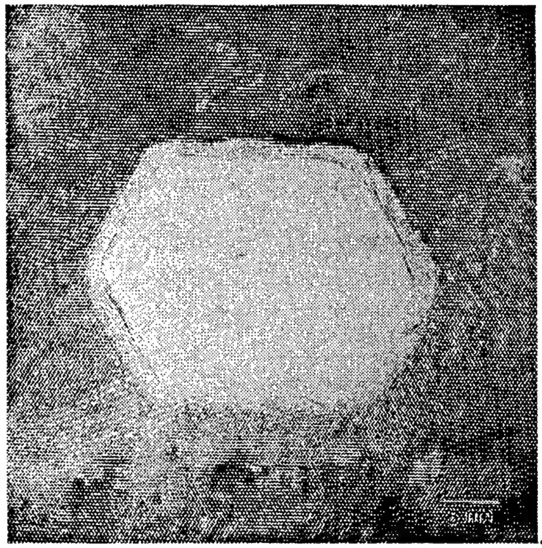

Fig. 3 Plan view TEM image of a nanotube in GaN/Al_2O_3.

The defect is an empty cylinder with diameter of between 10 and 80 nm propagating along the c-axis (in this case c-axis is also the growth direction). The density of nanotubes in GaN is in the 10^4-10^6 cm^{-2} range but was observed to increase in the AlGaN alloys. Nanotubes are almost always associated with dislocations either of screw or edge character. It is expected that nanotubes can have a significant impact of the leakage currents and breakdown voltages of nitride p-n junctions. Nanotubes terminate at the free surface of a layer forming a crater with diameter between 200 and 700 nm (Fig. 4).

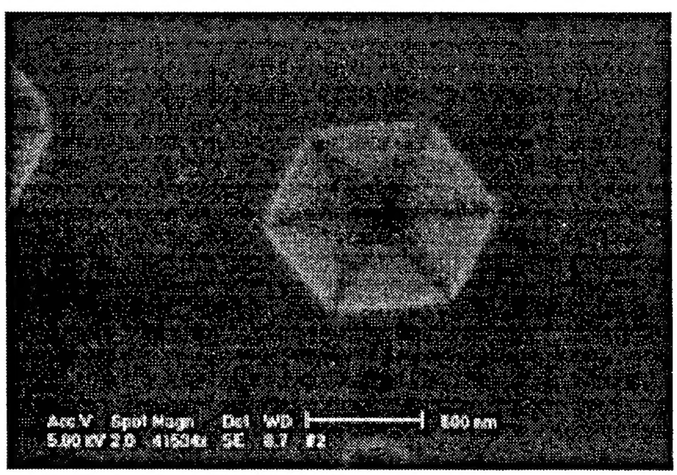

Fig. 4. SEM image of nanotube crater of $Al_{0.2}Ga_{0.8}N$ layer surface.

The densities of surface craters are higher in layers with increased aluminum concentration and can reach 10^8 cm^{-2} in $Al_{0.5}Ga_{0.5}N$. This correlation is thought as a second order effect. Increase of aluminum content of the film causes increased oxygen concentration as measured by Secondary Ion Mass Spectroscopy reaching 10^{20} cm^{-3} for 50% Al. At such high contamination levels, it is likely that aluminum oxide inclusions an form during the layer growth starting the nanotube and leading to crater formation.

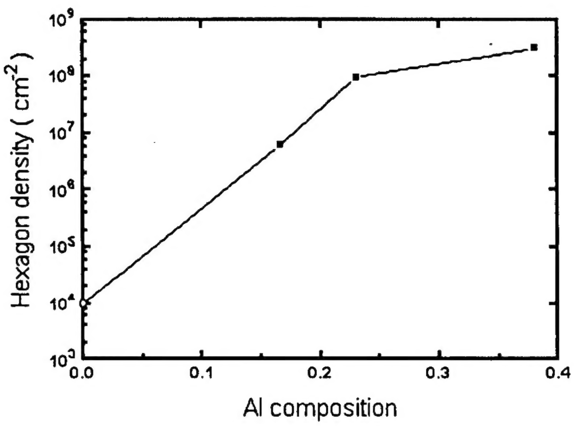

Fig. 5. Change of hexagon density as a function of Al composition.

Structural defects in SiC substrates

As a related subject we have investigated structural defects in SiC substrates used for nitride deposition. An important defect observed and reported for the first time was a polytype boundary between 6H and 15R SiC polytypes. The boundary is induced by a difference in stacking sequence along the c-axis and is formed by arrays of dislocations lying in the basal planes as shown in Fig. 6. Similar defects are expected at the SiC/GaN interfaces and possibly between cubic and hexagonal nitrides themselves.

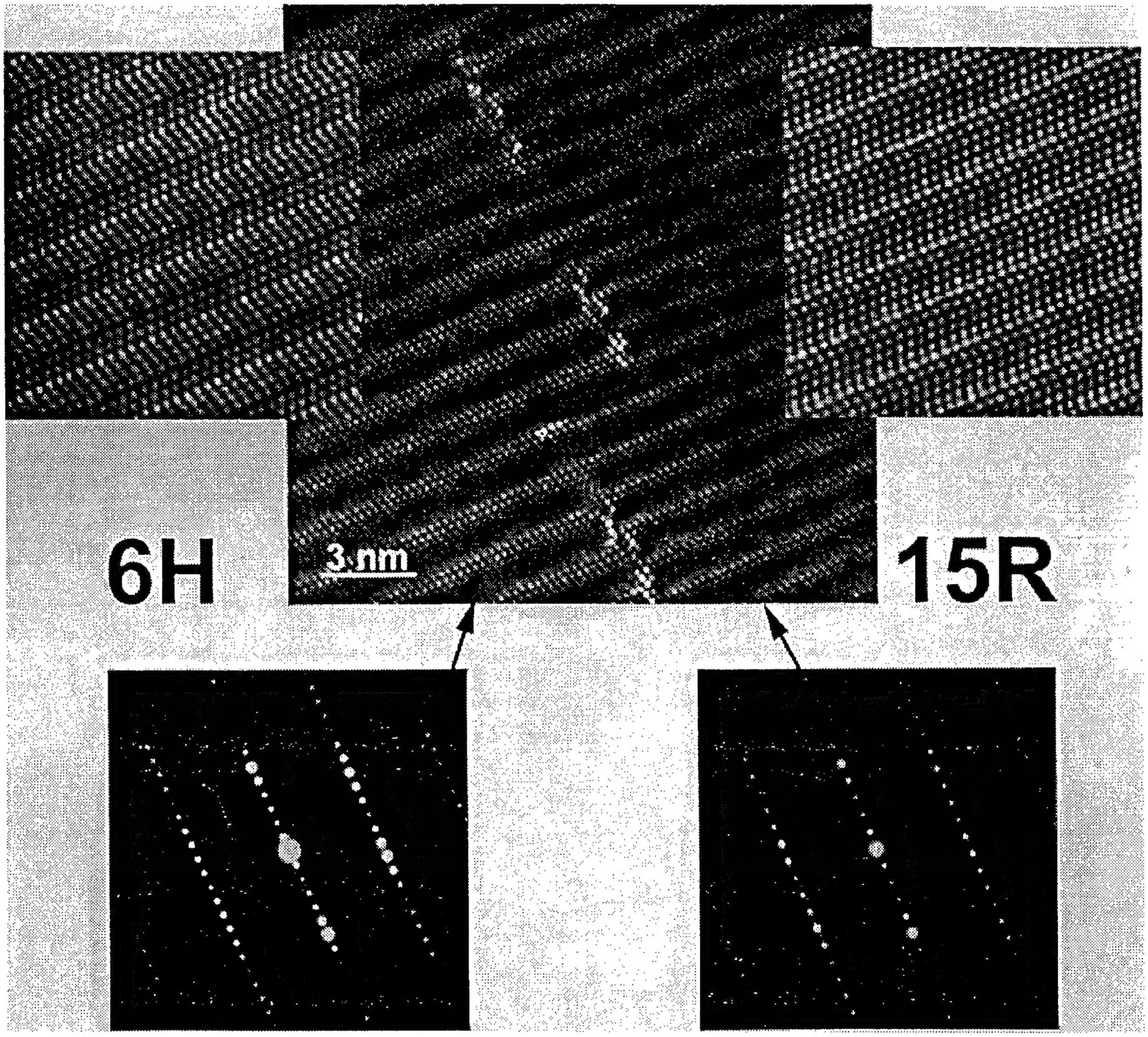

Fig. 6 Center: close-up of 6H-15R polytype interface. The stacking sequences of 6H and 15R as determined from higher magnification insets and selective area diffraction patterns.

Summary

A significant progress in understanding the growth mode of gallium nitride films on sapphire was achieved through the analysis of extended defects by Transmission Electron Microscopy. GaN domain structure was observed for the first time and interpreted as due to early nucleation stages of film growth. New type of defect, namely nanotubes, have been discovered and their densities correlated with presence of intentional dopants and oxygen contaminants.

Publications

1. “Microstructural characterization of a-GaN films grown on sapphire by organometallic vapor phase epitaxy”, W. Qian, M. Skowronski, M. De Graef, K. Doverspike, L. B. Rowland, and D. K. Gaskill, Appl. Phys. Lett. **66**, 1252 (1995)

2. “Observation of nanopipes in a-GaN crystals”, W. Qian, M. Skowronski, K. Doverspike, L. B. Rowland, and D. K. Gaskill, J. Crystal Growth **151**, 396 (1995)

3. "Open-core screw dislocations in GaN epilayers observed by scanning force microscopy and high-resolution transmission microscopy", W. Qian, G. S. Rohrer, M. Skowronski, K. Doverspike, L. B. Rowland, D. K. Gaskill, Appl. Phys. Lett. **67**, 2284 (1995)

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7. “HRTEM characterization of 6H-15R polytype boundaries in silicon carbide grown by physical vapor transport”, E. K. Sanchez, M. De Graef, W, Qian, and M. Skowronski, Mat. Res. Soc. Symp. Proc. **442**, 655 (1997)

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9. "High resolution x-ray diffraction analysis of GaN-based heterostructures grown by OMVPE", M. S. Goorsky, A. Y. Polyakov, M. Skowronski, M. Shin, and D. W. Greve, Mat. Res. Soc. Symp. **449**, 489 (1997)

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Interactions and collaborations

Dr. W. C. Mitchel, Air Force Research Laboratory, investigation of electrically active defects in AlGaN films
Maj. M. Estes, Air Force Research Laboratory, processing of UV solar blind photodetectors
Dr. D. K. Gaskill, K, Doverspike, L. B. Rowland, Naval Research Laboratory, identification of extended defects in GaN/Al_2O_3 layers
Dr. K. Jones, Army Research Laboratory, investigation of AlGaN contamination by Secondary Ion Mass Spectroscopy

Inventions/Patent Disclosures

None to date.